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# Characterizing Radiation-Aged Polysiloxane-Silica Composites: Identifying Changes in Network Topology via $^1$H NMR

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## Abstract

Characterizing and quantifying changes in elastomeric materials upon exposure to harsh environments is important in the estimation of device lifetimes. Nuclear magnetic resonance (NMR) spectroscopy has been used effectively in the analysis of such materials and has proved to be both sensitive to micro- and macroscopic changes associated with material "aging." Traditional analyses, however, rely on empirical formulae containing a large number of (often arbitrary) independent variables. This ambiguity can be circumvented largely by developing models of NMR observables that are based on basic polymer physics. We compare two such models, one previously published and one derived herein, along with empirical expressions that describe the proton transverse magnetization decay associated with complex polymer networks. One particular extracted parameter, the proton-proton residual dipolar coupling (RDC), can be directly related to network topology, and a comparison of the extracted RDCs reveals high consistency among the models. An expression derived from the properties of a static Gaussian chain can minimize the number of parameters necessarily to describe the solid-like, networked proton population to a single independent parameter, the average residual dipolar coupling, $D_{avg}$.

*Key words:* polymers, soft solids, NMR, residual dipolar coupling, mathematical modeling, parameter identification
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# 1  Introduction

Polysiloxane-based composites have been particularly attractive as structural materials due to a relatively large, tunable range in shear modulus upon milling with fumed silica, even at relatively low filler mass fractions. In practical application, however, these materials are often exposed to harsh chemical, physical, mechanical, and radiological environments that ultimately limit useful device lifetimes through irreversible changes in constituent components. The assessment of damage, particularly for elastomeric materials, is often done be monitoring changes in macroscopic structural properties (e.g., shear and storage moduli). These methods are often inherently destructive and typically afford an average measurement over the entire sample. In situations where these materials are scarce, sensitive, or otherwise difficult to attain in any quantity, there exists a need for analytical techniques to be sensitive to subtle changes in a non-destructive, non-invasive capacity. Perhaps most essential for engineering applications is the existence of intuitive analytical methodologies from which one can extract physically meaningful parameters from experimental data yet are simple to implement in practice while containing significant scientific rigor in their foundation.

Nuclear magnetic resonance spectroscopy (NMR) has been utilized effectively over the last few decades for both fundamental and applied studies of polymer-containing materials. Elastomeric materials form one case study for the efficacy of NMR in addressing fundamentals issues of polymer physics. Elastomeric composite materials exhibit both physical and chemical junctions (from e.g., surface-polymer interactions and chain crosslinking, respectively) that form a long-range network topology. This physical structure imposes restrictions on individual polymer segment motions, creating the inherently anisotropic dynamical nature of these materials. NMR exploits the anisotropic nature of various intra- and internuclear interactions to quantify local chain fluctuations over a wide range of motional time-scales, from discrete monomer motions to reptation and bulk diffusion. One observable that is particularly relevant is the *tranvserse decay* of the proton NMR signal. This decay, usually measured by stroboscopic sampling of the proton NMR signal during a repeating cycle of pulses, is governed by the residual proton-proton homonuclear dipolar coupling (RDC) between protons on polymer chains. This magnetic dipole-dipole interaction between protons is partially averaged by molecular motion; in network elastomers, the entanglements between chains and chain interaction with filler surfaces act as tethers so that the residual couplings forms an indirect measurement of entanglement density.

We have used previously proton transverse magnetization ($T_2$) decay to develop a correlation of a particular NMR derived quantity, the proton homonuclear dipolar second moment, to the shear modulus in PDMS-silica composites

and have demonstrated its use in the spatial resolution of macroscopic heterogeneities via NMR imaging techniques (Mayer et al., 2007). In analyzing our previous NMR data, several proton populations were spectroscopically identified, but it remains unclear if these populations correspond to any physically meaningful proton domains. Ultimately, the functional form chosen to describe proton $T_2$ decay, from which dipolar second moments were derived, became an ansatz chosen for simplicity and apparent fidelity to the data. Considering the heterogeneity of proton dynamics in networked polymers, one surmises that there exists a continuum of dipolar second moments, in contrast to the assertion of a distinct second moment for bulk network protons, a different second moment for protons on tightly silica-adsorbed chains, and others, perhaps, for weakly bound species. While a continuum model may be more physically appealing, the latter scenarios provide excellent fits to experimental data.

Previous workers have developed expressions for the transverse decay of protons on polymer chains, in polymer networks, etc., based on well-established ideas common in polymer physics. Most notably is a function that was applied to poly(styrene-co-butadiene) elastomers well above the glass transition temperature, $T_g$ (Sotta et al., 1996). These workers recast the spatially dependent terms of the homonuclear dipolar Hamiltonian in terms of the Gaussian distribution of the polymer end-to-end vector. The transverse decay associated with solid-like domains represents inhomogeneous line broadening of the proton lineshape, and though these interactions are weak, the investigators are able to correlate them to structural moduli of these elastomers.

In this article we seek to assess several expressions for the transverse decay of proton magnetization for a complex PDMS-based elastomer subjected to a range of $\gamma$-irradiation exposures. These materials have been examined in several other studies but in a more phenomenological fashion (e.g., Maxwell and Balazs, 2002; Maxwell et al., 2005; Mayer et al., 2007). Here we apply the function mentioned above (Sotta et al., 1996), a similar function derived herein, and an expression derived assuming an ansatz distribution of dipolar couplings. The extracted parameters will be compared to each other and to trends published previously in the literature. The utility and efficacy of these expressions in describing $T_2$ decay in complex elastomeric materials is considered.

## 2 Theory

We first present an abbreviated derivation of Eq. 8 from Sotta et al. (1996), which we will refer to as, $M_S(t)$, which represents the total $^1$H transverse magnetization of the spin system. Note that the subscript $S$ refers to the initial of that main author's last name. The authors take the inhomogeneous

component of the time evolution of the transverse magnetization (FID) and recast it in terms of the Gaussian distributed end-to-end vector of a static polymer chain. Convolution of the FID (neglecting homogeneous $T_2$ terms) with the Gaussian distribution yields the normalized, closed form expression

$$\frac{M_S(t)}{M_0} = \text{Re}\left[\left(1 - \frac{2}{3}i\frac{k}{N}Dt\right)^{-\frac{1}{2}}\left(1 + \frac{1}{2}i\frac{k}{N}Dt\right)^{-1}\right] \tag{1}$$

where $M_0$ is the initial transverse magnetization, $N$ is related to the number of repeat units between crosslinks (i.e. a measure of interjunction segment length), $k$ is a geometrical factor (equal to, e.g., $\frac{3}{5}$ for a freely jointed chain (Sotta and Deloche, 1990)), and $D$ is the homonuclear dipolar coupling strength given by

$$D = \frac{\mu_0}{4\pi}\frac{\gamma^2\hbar}{r^3} \tag{2}$$

where $\gamma$ is the proton gyromagnetic ratio, and $r$ is the internuclear distance. Note that since $D$ represents the *static* dipolar coupling strength (a constant for a given distance, $d$) from known monomer geometry, the sole parameter determining $M_S(t)$ is $N$, the effective mesh length of the network. This parameter can also be thought of as a scaling factor by which the dipolar coupling is reduced as a result of motional averaging over that length scale. This reduced coupling is referred to as the *residual* dipolar coupling (hereafter referred to as the RDC) constant and represents the coupling strength after averaging by fast, local segmental chain motions (i.e. those motions experienced by polymer chains despite the presence of the network topological constraints).

A similar expression can be derived that employs the so-called second moment approximation (Kimmich, 1997). This assumption assumes that $D^2N^2t^2 \gg 1$, equivalent to the ansatz that strong dipolar couplings dominate the decay at short times. In this case we can write the basic transverse decay of proton magnetization as

$$\frac{M(t)}{M_0} = \exp\left(-\frac{9}{20}\left(\frac{k}{N}D\right)^2 t^2\right) \tag{3}$$

where all the constants and $N$ have been collapsed into a single parameter, the dipolar second moment, $M_2$. Convolution in a similar manner as Eq. 1 yields (see Appendix I)

$$\frac{M_M(t)}{M_0} = \frac{5^{\frac{3}{4}}}{2\sqrt{2}\left(\frac{k}{N}Dt\right)^{\frac{3}{2}}}\text{U}\left(\frac{3}{4}, \frac{1}{2}; \frac{5}{\left(2\frac{k}{N}Dt\right)^2}\right). \tag{4}$$

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where $U(a, c; x)$ is the confluent hypergeometric function of the second kind, and the subscript $M$ refers to the present author's name. Note that by recasting the Gaussian end-to-end vector distribution in terms of the quantity $\frac{D}{N}$, the new distribution of residual second moments, $P_M$, can be represented in terms of a Gamma distribution of $D_{res}$, or

$$P_M(D_{res}) = \frac{2}{\sqrt{\pi}} \left( \frac{3}{2 \frac{k}{N} D} \right)^{\frac{3}{2}} \sqrt{D_{res}} \exp\left( -\frac{3}{2} \frac{D_{res}}{\frac{k}{N} D} \right) \tag{5}$$

for $D_{res} \geq 0$. We will return to this important result below. Additionally, we will refer to the quantity $\frac{k}{N} D$ as $D_{avg}$ for notational simplicity.

Lastly we will give an alternative expression that is based on an assumption that the NMR behavior of the network is governed by a Gaussian distribution of residual dipolar couplings. This is derived in the same manner as Eq. 4, but using instead the normalized distribution

$$P_G(D_{res}) = \sqrt{\frac{2}{\pi}} \frac{1}{\sigma} \left[ 1 + \mathrm{erf}\left( \sqrt{\frac{D_{avg}^2}{2\sigma^2}} \right) \right]^{-1} \exp\left( \frac{-(D_{res} - D_{avg})^2}{2\sigma^2} \right) \tag{6}$$

for $D_{res} \geq 0$. Following Appendix I the expression for the decay transverse magnetization (with subscript $G$ for "Gaussian") is

$$M_G(t) = \exp\left( \frac{-\frac{9}{20} D_{avg}^2 t^2}{1 + \frac{9}{10} \sigma^2 t^2} \right) \left( 1 + \frac{9}{10} \sigma^2 t^2 \right)^{-\frac{1}{2}}$$

$$\times \left[ \frac{1 + \mathrm{erf}\left( \sqrt{\frac{5 D_{avg}^2}{10\sigma^2 + 9\sigma^4 t^2}} \right)}{1 + \mathrm{erf}\left( \sqrt{\frac{D_{avg}^2}{2\sigma^2}} \right)} \right]. \tag{7}$$

These three expressions, Eqs. 1, 4, and 7, will be investigated along the phenomenological superposition of moments used in Mayer et al. (2007):

$$\frac{M_E(t)}{M_0} = x_1 \exp\left( -\frac{9}{20} D_{res}^2 \tau^2 \right) + \sum_{i=2}^{4} x_i \exp\left( -\frac{\tau}{T_{2,i}} \right) \tag{8}$$

normalized such that $\sum_{i=1}^{4} x_i = 1$. Here the subscript $E$ denotes that that function is "empirical." This expression represents a sum of discrete second moments, each relating to a different type of proton environment. Finally, all decay expressions will be assumed to be properly normalized, omitting further reference to $M_0$.

## 3 Experimental

### 3.1 Sample preparation

The PDMS-based material (Honeywell, Kansas City) is a random copolymer containing approximately 90.7 wt% PDMS, 9.0 wt% PDPS (poly(diphenylsiloxane)), and a small percentage of methylvinylsiloxane monomeric units that act as alkyl crosslinking units for initial network formation upon curing. The fillers used to formulate the composites were a fumed silica, Cab-O-Sil M7D (NuSil Corp., Carpenteria, CA) and a porous, precipitated silica, HiSil 233 (PPG Industries Inc., Pittsburg, PA). They have BET-determined surface areas of approximately 200 m$^2$/g and 150 m$^2$/g, respectively, as reported by their manufacturers. Final amounts of filler in composite are 21.6 wt% Cab-O-Sil and 4.0 wt% HiSil. A detailed description of elastomer synthesis can be found elsewhere (Maxwell and Balazs, 2002), but it is important to note that after their preparation, the samples were exposed to five different levels of $\gamma$-irradiation in air (1, 5, 10, 25, and 50 MRad, via a $^{60}$Co source at 1.2 MeV).

### 3.2 NMR

$^1$H NMR was conducted on an Apollo spectrometer (Tecmag, Houston, TX) at a magnetic field of 7.03 Tesla (corresponding to a proton Larmor frequency of 299.32 MHz). The experiments were performed at 25°C under static conditions, as the highly mobile networks provided significantly narrower proton line-widths than those typically seen with polymeric materials. Additionally, as room temperature is significantly above the glass transition temperature of PDMS ($T > T_g + 50$°C), chain mobility will be not dominated by thermal motion, but instead by the topological constraints. Data were collected using a Carr-Purcell-Meibloom-Gill (CPMG) pulse sequence (with CYCLOPS phase cycling),

$$\left(\frac{\pi}{2}\right)_x - [\tau_E - \pi_y - \tau_E - acquire]_N \tag{9}$$

where $x$ and $y$ indicate the radio frequency phases of the pulses with angles $\pi/2$ and $\pi$, respectively, and $\tau_E$ is the inter-pulse spacing. The sequence within the brackets is repeated $N$ times such that $N$ echoes are acquired in a single experiment. This method is efficient since the entire echo train can be recorded in a single experiment. More importantly, quickly refocussing the magnetization (i.e. setting $\tau_E \sim 100\mu$sec) prevents, to a large degree, coherence loss due to competing relaxation pathways that would otherwise contribute largely to

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signal attenuation. A typical experiment consists of 512 echoes and requires on the order of 15 minutes to complete given a repetition delay of 10 seconds and 64-128 signal averages.

## 4   Results and Discussion

Fig. 1 compares the predicted decay envelopes according to Eqs. 1, 4, and 7. The value of $D_{avg}$ has been fixed at 1 (with arbitrary units of inverse time) for all curves. The standard deviation for $M_G(t)$ has been fixed to that of the Gamma distribution of order $\frac{3}{2}$, i.e., $\sigma = \sqrt{\frac{2}{3}} D_{res}$. This measure is to ensure that the curves can be compared directly.

Note the strong similarities between $M_S(t)$ and $M_M(t)$ in both their absolute shape and their limiting behavior. At short times, $D_{avg}^2 t^2 \ll 1$, both functions have a Gaussian behavior,

$$M_S(t) \approx 1 - \frac{1}{6} D_{avg}^2 t^2 \tag{10}$$

$$M_M(t) \approx 1 - \frac{3}{4} D_{avg}^2 t^2. \tag{11}$$

The larger prefactor in Eq. 11 reflects the fact that the second moment approximation weights preferentially stronger dipolar couplings. Additionally, both functions display identical behaviors at long times, $D_{avg}^2 t^2 \gg 1$,

$$M_S(t) = M_M(t) \approx (D_{avg} t)^{-3/2} \tag{12}$$

It appears then, that the application of the second moment approximation does not significantly change the qualitative shape of the decay envelope vis-a-vis $M_S(t)$. Note that for a given set of data, however, any extracted fits using $M_M(t)$ will yield consistently lower values of $D_{avg}$ due to the larger prefactor.

Previous workers have recognized that the quantity $D_{avg}^2/3$ is contained within Eq. 10 and is the van Vleck second moment, $M_2$, of the residual dipolar interaction (Sotta et al., 1996). To "correct" our extracted values of $D_{avg}$ such that they are consisent with those from $M_S(t)$, we have simply to multiply by a factor of $\sqrt{2/9}$. Of course, this factor accounts for only the short-time, asymptotic behavior and, as such, it will only be expected to apply under the conditions used in deriving Eqs. 10 and 11. To minimize globally the difference between $M_S(t)$ and $M_M(t)$, one can introduce a numerical factor of approximately 0.57. This value maintains the difference below 5% overall. Both the effects of the $\sqrt{2/9}$ and 0.57 correction factors are shown in Fig. 2.

There exists little visual similarity between the Gaussian-based expression, $M_G(t)$, and the other two functions as plotted in figure **??**. Recall that the standard deviation, $\sigma$, of $M_G(t)$ can be set independently, and as such it was set to the value fixed by the gamma distribution of RDCs from Eq. 5. Presumably, however, some combination of $D_{avg}$ and $\sigma$ can reproduce well the curves generated by $M_S(t)$ and $M_M(t)$. The use of these combinations will be pursued in light of the data (*vide infra*), but no straight-forward mathematical comparisons can be established (as was the case with Eqs. 1 and 4), as both short- and long-time behavior are highly coupled to the ratio of $D_{avg}$ to $\sigma$.

The goal of this work is to provide a simple, intuitive method of the analysis of transverse decay data from these complex elastomeric materials. Minimization of the number of adjustable parameters needed to fit the data allows for efficient, robust data analysis and interpretation. In our previous publication, Mayer et al. (2007), Eq. 8 was used to fit the decay envelopes; with seven independent variables, however, any physically meaningful interpretation of the extracted parameters and their trends was difficult. The present functions, assuming a distribution of residual dipolar couplings (as opposed to a single *effective* coupling constant), as it will be shown, can account quite well for heterogeneous coupling environments and simultaneously produce physically meaningful data.

A fit of Eqs. 1, 4, 7, and 8 to our data starts with an assessment of long-time decays present in all samples. These decays are well-known (ref) to derive from those portions of the sample that experience rapid, liquid-like motions. This would include, for example, motionally unrestricted, highly flexible dangling chain ends or even, perhaps, a labile water or solvent population. In all of our data we find one or two such components. These liquid-like, slowly decaying signals (echo times greater than 25 msec) are effectively invariant among the samples studied, and can be simply accounted for by using additional $\exp(-t/T_2)$ functions to fit the data. With the addition of these terms the total number of independent variables is five when using Eqs. 1 and 4 and six when using Eq. 7. Even though this appears to not be a significant improvement in terms of the size of the variable space, the liquid-like components can be treated independently. We find that there is no dependence of the extracted $T_2$ values on the model chosen to fit the data, in accordance with the expectation that the model chosen to represent the solid-like (fast-decaying) component should not affect the outcome of the analysis for the liquid-like domains. There is also little statistical difference among the values for the size of the proton populations described by Eqs. 1, 4, and 7 for a given dosage. Ultimately, then, our primary concern is the description of the short-time decay described by the equations presented earlier, and we choose to ignore the additional $T_2$ terms throughout the rest of the manuscript.

Fig 3. shows decay envelopes for the pristine (unexposed), 1 MRad, and 50

MRad samples to approximately 1% of the initial magnetization intensity. Figure 4 shows the fit and its deconvolution for the 50 MRad sample using Eq. 4. Table C.1 shows the results from fitting the decay curves for the pristine and irradiated samples using Eq. 4 with *two* $T_2$ terms to account for the long-time decay.

Fig. 5 shows graphically the $D_{res}$ values extracted using the three models and those from the single-valued model from Mayer et al. (2007). For the Gaussian-based values, the plotted parameter is $\sigma$ and not the average RDC. In addition to the raw values extracted using Eq. 1, included are the "corrected" values using the factor of 0.57 discussed above. All the values fall within the same range and produce the same quantitative trend: the elastomer softens at relatively low dosages, then stiffens (compared to the pristine sample) upon exposure up to 50 Mrad. This notion is based upon the fact that both the residual dipolar coupling strength and the shear modulus are both dependent on the reciprocal of the average chain length between crosslinks (i.e. the crosslink density).

The extracted parameters from all four expressions duplicate a trend identical to that of shear modulus as a function of dosage determined via swelling experiments (Chien et al., 2000). Ultimately, then, any of the expressions discussed above can be used to determine an average RDC. The added benefit of using e.g., Eq. 4, however, is that a distribution of RDCs can be directly visualized using Eqs. 5 and 6, as shown in Fig. 6. Eq. 5 is applicable to not only the gamma-based model but also to Eq. 1 since they are derived from the same basic idea.

Note that the distributions derived from Eq. 7 mimic quite closely those from Eq. 4 (a fact that holds for all six samples). It is interesting that the distribution given in Eq. 6 is a pure anstaz and that it reproduces well the general shape of the gamma distribution. This observation lends some support to the idea that the transverse decay of protons in polymer networks might be well described by static chain statistics. This is in contrast to recent work that has used regularization techniques to back out distributions in rubbers that are surprisingly sharp and homogeneous. Nevertheless, the consistency of the extracted data suggests equal efficacy of these expressions in assessing residual dipolar coupling in potentially complex systems while minimizing subjective fitting procedures employing a large number of free variables.

## 5   Conclusion

The engineering of new materials requires methods that can analyze data in both efficient and physically meaningful way. The expressions investigated above all produce similar results for the residual dipolar coupling strength and

radiation effects thereof in PDMS-based materials. These close-formed expressions, particular that based on the use of the second moment approximation, portend simple extraction of parameters without the use of regularization techniques (Saalwächter, 2007) or numerical inverse Laplace transformations (Song et al., 2008). Coupling these results with those established previously provides a simple yet powerful way for determining subtle changes in soft materials due to the wide range of harsh chemical, physical, mechanical, and radiological environments that ultimately limit useful device lifetimes through irreversible changes in constituent components.

## 6   Acknowledgments

## A   Appendix I

Derivation of Eq. 4 begins by using the equality (Sotta and Deloche, 1990)

$$\frac{D_{res}}{D_{stat}} = \frac{3}{5}\frac{r^2}{N},\tag{A.1}$$

which represents the degree of averaging of the dipolar interaction (i.e. order parameter) by fast intrasegment motions of chain constituents. Recasting the typical Gaussian distribution of the squared end-to-end vector, $r^2$, in terms of $D_{res}$, one arrives at a gamma probability function of order 3/2.

$$P_M\left(D_{res}\right) = \frac{2}{\sqrt{\pi}}\left(\frac{3}{2D_{avg}}\right)^{\frac{3}{2}}\sqrt{D_{res}}\exp\left(-\frac{3}{2}\frac{D_{res}}{D_{avg}}\right)\tag{A.2}$$

Our goal is to obtain an expression for the solid-like transverse magnetization decay governed by the continuum of RDCs from Eq. A.2. This can be simply by integrating the distribution with a kernel function given by Eq. 3 over the interval of all positive values for $D_{res}$. We define this convolution as $M_M\left(t\right)$ and therefore seek an analytical solution to

$$M_M(t) = \int_0^\infty S\left(t, D_{res}\right) P_M\left(D_{res}\right) \mathrm{d}D_{res} \tag{A.3}$$

$$= \frac{2}{\sqrt{\pi}} \left(\frac{3}{2D_{avg}}\right)^{\frac{3}{2}} \int_0^\infty \exp\left(-\frac{9}{20} D_{res}^2 t^2\right)$$

$$\sqrt{D_{res}} \exp\left(-\frac{3}{2} \frac{D_{res}}{D_{avg}}\right) \mathrm{d}D_{res}. \tag{A.4}$$

Collapsing all constants above yields an integral of the form

$$A \int_0^\infty \sqrt{x} \exp\left[-\left(Bx + Cx^2 t^2\right)\right] \mathrm{d}x \tag{A.5}$$

which can be solved more readily by a variable substitution. By redefining $x$ to be $\ln(y)$, we have

$$A \int_1^\infty y^{-(1+B)} \sqrt{\ln y} \exp\left[-C\left(\ln y\right)^2 t^2\right] \mathrm{d}y. \tag{A.6}$$

The closed-form solution can be written in terms of the confluent hypergeometric function, $U(a, c; x)$. Substituting back in all relevant constants, the solid-like transverse decay for a gamma distribution of $D_{res}$ becomes Eq. 4:

$$M_M(t) = \frac{5^{\frac{3}{4}}}{2\sqrt{2}\left(D_{avg}t\right)^{\frac{3}{2}}} U\left(\frac{3}{4}, \frac{1}{2}; \frac{5}{\left(2D_{avg}t\right)^2}\right). \tag{A.7}$$

Note that we are not required to convert back into the $x$-basis because $x$ was the variable of integration.

To derive Eq. 7, we begin with an Gaussian RDC probability function, $P_G$, given by

$$P_G\left(D_{res}\right) = A_0 \exp\left(\frac{-\left(D_{res} - D_{avg}\right)^2}{2\sigma^2}\right) \tag{A.8}$$

where $D_{avg}$ is defined as above, $\sigma$ is the standard deviation of the distribution, and $A_0$ is an arbitrary constant. We use the decay expression under the second moment approximation as the kernel function again (Eq. 3) and desire a simplification to the expression

$$M_G(t) = \int_0^\infty S(t, D_{res}) P_G(D_{res}) \, \mathrm{d}D_{res} \Big/ \int_0^\infty P_G(D_{res}) \, \mathrm{d}D_{res} \tag{A.9}$$

$$= \int_0^\infty \exp\left(-\frac{9}{20} D_{res}^2 t^2\right) \exp\left(\frac{-(D_{res} - D_{avg})^2}{2\sigma^2}\right) \mathrm{d}D_{res}$$

$$\Big/ \int_0^\infty \exp\left(\frac{-(D_{res} - D_{avg})^2}{2\sigma^2}\right) \mathrm{d}D_{res} \tag{A.10}$$

Note that we are forced to integrate over physically possible values of $D_{res}$ making normalization essential. The solution to this integral can be written as

$$M_G(t) = \exp\left(\frac{-\frac{9}{20} D_{avg}^2 t^2}{1 + \frac{9}{10}\sigma^2 t^2}\right) \left(1 + \frac{9}{10}\sigma^2 t^2\right)^{-\frac{1}{2}}$$

$$\times \left[\frac{1 + \mathrm{erf}\left(\sqrt{\frac{5 D_{avg}^2}{10\sigma^2 + 9\sigma^4 t^2}}\right)}{1 + \mathrm{erf}\left(\sqrt{\frac{D_{avg}^2}{2\sigma^2}}\right)}\right]. \tag{A.11}$$

We must also make Eq. 16 reflect the boundary conditions of the problem. The normalization prefactor, $A_0$, in that expression is given by

$$A_0 = \sqrt{\frac{2}{\pi}} \frac{1}{\sigma} \left[1 + \mathrm{erf}\left(\sqrt{\frac{D_{avg}^2}{2\sigma^2}}\right)\right]^{-1}. \tag{A.12}$$

Substituting Eq. A.12 into Eq. A.8 yields Eq. 6.

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## B    Figure Captions

*Figure 1.* Comparison of Eqs. 1, 4, and 7. $D_{avg}$ has been fixed to 1 for all three curves. The standard deviation of the Gaussian derived function, $M_G(t)$, has been fixed to that of the gamma distribution from $M_M(t)$, $\sigma = \sqrt{\frac{2}{3}}D_{avg}$. The abscissa is in units of arbitrary time. Note, however, that for times greater than 10, the decay is shown in log-log space to demonstrate the asymptotic behavior of the functions.

*Figure 2.* Residual comparison between Eqs. 1 and 4: $M_M(t) - M_S(t)$. The factor $f$ has been applied to the product $D_{avg}t$ in Eq. 4. The residuals are globally minimized at $f \approx 0.57$, and it is clear that $M_M(t)$ decays faster for short times then slows down, being taken over by the decay of Eq. 1 at $t \approx 3$. The abscissa is in units of arbitrary time, and $D_{avg}$ has been set to unity.

*Figure 3.* $T_2$ decay curves for pristine, 1 MRad and 50 MRad samples at 299.32 MHz. The delay between echo acquisitions is 568 $\mu$sec with a $\pi/2$ pulse length of 2.5 $\mu$sec. The solid-like decay dominates at short echo times and is shown in detail in the inset. This quick decay accounts for the majority of the proton population with a fraction, $x$, of about 0.73 on average.

*Figure 4.* Decay data from 50 MRad sample with short-time inset. The black solid curve represents the total fit using an exponential decay in conjuction with the gamma-based expression from Eq. 4. The gray solid and dashed lines denote the deconvolved contributions to the total decay envolope. Another exponential term would be needed to accurately capture the decay past 50 msec, but the fidelity of the fit to the data at lesser times is high.

*Figure 5.* A comparison of selected parameters from Table C.1. Plotted are the $D_{avg}$ values extracted using Eqs. 1, 4, 7, and 8. For the Gaussian-derived model, $\sigma$ is plotted. Also plotted are the "corrected" values from Eq. 1: the extracted $D_{avg}$ values have been multiplied by 0.57 as discussed earlier.

*Figure 6.* Comparison of the gamma- and Gaussian-derived distributions from the parameters given in Table C.1. Depicted are only those from the pristine, 1 MRad, and 50 MRad.

## C   Tables

Table C.1

Extracted parameters using Eqs. 1, 4, and 7 as a function of radiation dosage in MRad. Note the addition of two $\exp\left(-t/T_2\right)$ terms to account for the liquid-like decay. The average error associated with the fitting procedure is shown only for the pristine (0 MRad) sample but is representative of all six samples studied.

| | | $M_S(t)$ (Eq. 1) | | | | |
|---|---|---|---|---|---|---|
| Dosage | $D_{avg}$ (Hz) | | $x_D$ | $T_{2,1}$ (msec) | $x_{T_{2,1}}$ | $T_{2,2}(\times 10^3)$ |
| 0 | $451 \pm 12$ | | $0.75 \pm 0.05$ | $30.4 \pm 2.8$ | $0.24 \pm 0.03$ | $4.2 \pm 4.6$ |
| 1 | 349 | | 0.70 | 30.2 | 0.29 | 6.1 |
| 5 | 432 | | 0.60 | 27.2 | 0.38 | 11.0 |
| 10 | 421 | | 0.69 | 26.3 | 0.30 | 5.4 |
| 25 | 504 | | 0.71 | 27.0 | 0.28 | 6.5 |
| 50 | 515 | | 0.75 | 27.8 | 0.24 | 8.3 |
| | | $M_M(t)$ (Eq. 4) | | | | |
| Dosage | $D_{avg}$ (Hz) | | $x_D$ | $T_{2,1}$ (msec) | $x_{T_{2,1}}$ | $T_{2,2}(\times 10^3)$ |
| 0 | $291 \pm 6$ | | $0.80 \pm 0.03$ | $35.9 \pm 1.8$ | $0.23 \pm 0.03$ | $4.5 \pm 3.6$ |
| 1 | 204 | | 0.74 | 30.2 | 0.31 | 6.4 |
| 5 | 207 | | 0.67 | 27.7 | 0.36 | 10.9 |
| 10 | 213 | | 0.77 | 29.5 | 0.27 | 6.4 |
| 25 | 297 | | 0.79 | 31.1 | 0.23 | 6.7 |
| 50 | 382 | | 0.79 | 28.1 | 0.20 | 8.4 |
| | | $M_G(t)$ (Eq. 7) | | | | |
| Dosage | $D_{avg}$ (Hz) | $\sigma$ (Hz) | $x_D$ | $T_{2,1}$ (msec) | $x_{T_{2,1}}$ | $T_{2,2}(\times 10^3)$ |
| 0 | $59 \pm 4$ | $290 \pm 13$ | $0.82 \pm 0.06$ | $33.0 \pm 1.8$ | $0.15 \pm 0.02$ | $32 \pm 9$ |
| 1 | 6 | 185 | 0.74 | 28.7 | 0.20 | 63 |
| 5 | $\sim 0$ | 239 | 0.69 | 25.6 | 0.25 | 56 |
| 10 | $\sim 0$ | 241 | 0.77 | 26.3 | 0.17 | 57 |
| 25 | 24 | 326 | 0.82 | 28.7 | 0.14 | 34 |
| 50 | 7 | 438 | 0.86 | 29.5 | 0.13 | 10 |

Inset axis labels: normalized intensity (y-axis), echo time (msec) (x-axis), with x-axis values 0, 5, 10, 15, 20, 25 and y-axis values 1, 0.1.

Main plot axis labels: normalized intensity (y-axis), echo time (msec) (x-axis), with x-axis values 0, 25, 50, 75, 100 and y-axis values 1, 0.1, 0.01.

Legend:
- 50 MRad data
- solid + liquid
- solid
- liquid